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A RAPID METHOD FOR DETERMINING ^{85}Kr IN ENVIRONMENTAL AIR SAMPLES

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Abstract

A RAPID METHOD FOR DETERMINING ^{85}Kr IN ENVIRONMENTAL AIR SAMPLES.

In support of the Environmental Protection Agency's mission of evaluating environmental insult, the Agency's Eastern Environmental Radiation Laboratory has developed a rapid method for determining ^{85}Kr in environmental air samples. Equipment and procedure used to separate ^{85}Kr from environmental air samples for liquid scintillation counting are described in detail. The procedure employs charcoal and molecular sieve cold traps, calcium sulphate, ascarite (NaOH preparation) and a titanium furnace (900°C) for the removal and separation of other air constituents from krypton. Air samples are spiked with $^{85}\text{Kr}^{10}$ to provide a direct determination of the krypton separation yield. This feature eliminates the need for expensive analytical equipment, such as a mass spectrograph for determining the purity of the final separation and the uncertainty in measuring krypton volumetrically when small amounts of other gases are present. The design of this system also eliminates the need for copper, cupric oxide and lithium furnaces which have been employed in other krypton separation systems. The system components are essentially all metal, thus eliminating many of the breakage problems encountered with glass systems. One cubic metre of air can be processed in about 4 h with 80 to 90% krypton recovery resulting in a 2-sigma error of the ^{85}Kr concentration of less than 10%. The processing time can be reduced if lower krypton recoveries can be tolerated. The procedure is well suited to monitoring environmental air samples with respect to nuclear facilities, such as nuclear reactors and fuel reprocessing plants.

The concentration of ^{85}Kr in the atmosphere is increasing [1] due mainly to the nuclear power industry. As this industry expands, the atmospheric concentrations of ^{85}Kr are expected to continue to increase [2]. The fuel reprocessing plants are the greatest contributors of ^{85}Kr to the atmosphere at the present time. As this occurs, the need for accurate concentration data will become more imperative in order to assess the radiation dose to the population and to predict future trends as the nuclear power industry expands. To date, the data on environmental ^{85}Kr concentrations are limited to a few locations, primarily commercial krypton separation plants.

The present methods for separating krypton from the other air constituents in order to analyze the radioactive krypton suffers from one or more of the following disadvantages: (a) time consuming, (b) uncertainty in measuring the volume of the separated krypton, (c) require expensive analytical instruments, e.g., mass spectrograph, to determine the krypton separation purity, and (d) maintenance problems, e.g. breakage of glass systems. This paper presents procedures and equipment diagrams of a system for separating krypton from environmental air samples which eliminates these disadvantages.

EQUIPMENT AND PROCEDURES

The procedure for separating krypton from the other air constituents (detailed procedure given in the Appendix) involves passing approximately one cubic meter of air, spiked with ^{83}mKr , through a charcoal trap at liquid nitrogen temperature (LN) and reduced pressure. This allows the greater part of the nitrogen and oxygen to pass through the trap while concentrating krypton and some of the other noble gases. The small amount of nitrogen that is retained by the charcoal is removed with a titanium furnace. The noble gases are transferred to a molecular sieve trap (LN) and fractionated cryogenically. The krypton is collected on a small amount of charcoal (LN) and subsequently collected in a glass liquid scintillation vial (LN).

Presented in Figures 1 and 2 are the schematic diagrams of a system for spiking air samples with ^{83}mKr and a system for separating krypton from air samples, respectively. The systems are constructed with copper tubing and brass ferrule-type fittings. The only glass in the systems are the flow meters, the liquid scintillation vials and the cold trap just before vacuum pump number one. Trap I is a 300-cm³ stainless-steel sample cylinder filled with 40-50 mesh activated coconut charcoal. Trap II is a 70-cm length of 3/4-inch (o.d.) stainless-steel pipe filled with 3.5 - 7 mesh titanium sponge. Trap III is a 345-cm length of 3/8-inch (o.d.) copper tubing filled with 50-60 mesh 5A molecular sieve. Trap IV is a 15-cm length of 3/16-inch (o.d.) copper tubing filled with 40-50 mesh activated coconut charcoal.

The ^{83}mKr generator (Figure 1) is contained in a 6-cm length of 3/8-inch (o.d.) copper tubing capped at one end. ^{83}mKr (1.86 h half-life) is the daughter of ^{83}Rb (83 d half-life) which is an impurity in ^{84}Rb (33 d half-life) solutions. Two cm³ of a ^{84}Rb

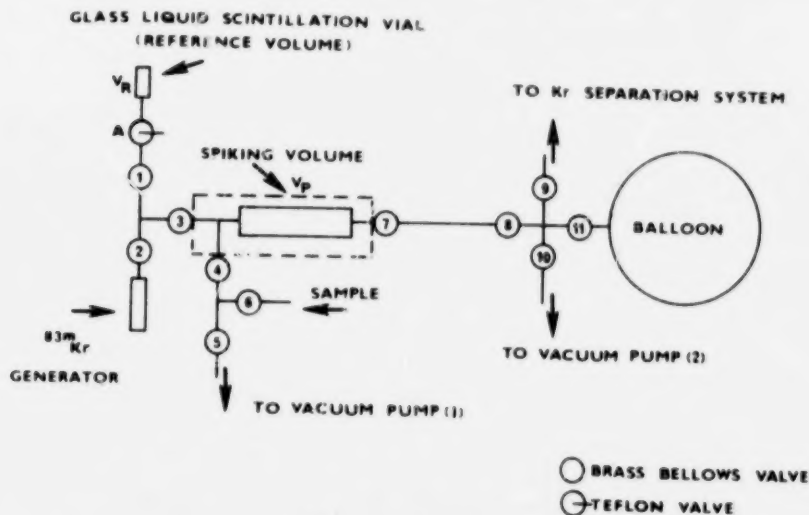


FIG. 1. Air spiking system.

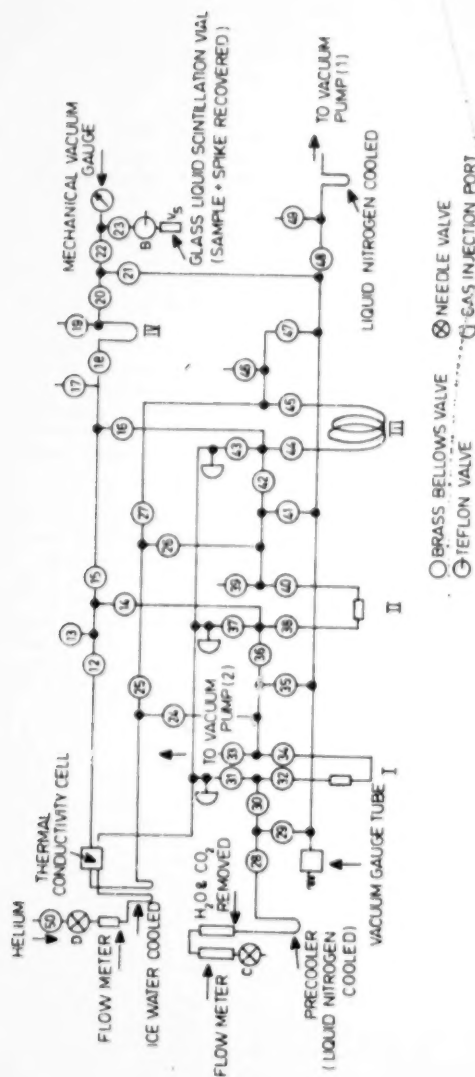


FIG. 2. Krypton separation system.

solution (approximately 0.1 mCi ^{83}Rb) that had gone through several half-lives was evaporated to dryness in the generator container. The container was plugged with cotton to prevent the escape of rubidium salt particles during the equilibration procedure.

DISCUSSION

The krypton separation system (Figure 2) is a modification of the system employed by Johns [3] in analyses of several gaseous radionuclides, including ^{85}Kr , which are produced in underground nuclear explosions. Separation yields in Johns' procedure are determined by the introduction of a known quantity of a stable element of the particular radionuclide involved. When analyzing for environmental levels of ^{85}Kr the stable element addition technique cannot be employed because the stable krypton contains a quantity of ^{85}Kr that was present in the air when the stable krypton was separated. Therefore, other methods of determining the separation yield or the purity of the separated krypton must be employed. Two techniques presently in use are (a) the volumetric measurement of the separated krypton gas [3] and (b) a mass spectrographic purity analysis of the separated krypton gas [4]. In the volumetric method there is always the uncertainty of the purity of the krypton separated. The spectrographic method involves expensive equipment that is not always available nor economically feasible in many laboratories.

The procedure presented in this paper alleviates the problems encountered with the volumetric and spectrographic techniques. These problems are overcome by spiking the air sample with ^{83m}Kr (1.86 h half-life) and determining the krypton separation yield. In this procedure small quantities of gases other than krypton can be tolerated as long as all the gases can be dissolved in the liquid scintillator and the contaminating gases do not contribute counts in the ^{85}Kr counting region or cause an undeterminable quenching effect. A previous study has shown that small quantities of air constituents do not cause a measurable quenching effect when counting ^{85}Kr [5].

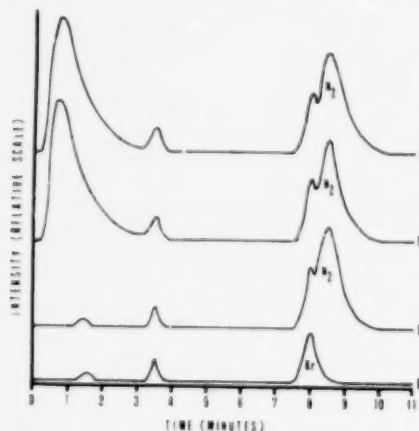


FIG. 3. Thermal conductivity cell response with time as the sample was removed from the molecular sieve trap at 0°C: (a) No furnace, (b) cupric oxide furnace, (c) copper metal furnace, and (d) titanium furnace.

The ^{83m}Kr generator, the reference volume (V_r) and the spiking volume (V_p) are all under vacuum, and at equilibrium the activity in V_p can be calculated from the activity in V_r and knowing the ratio of the two volumes. The purity of the ^{83m}Kr gas was checked by determining its half-life in V_r . A half-life of 1.88 h was calculated. This is compared to 1.86 h given in the reference [6].

In developing the present procedures, two additional furnaces were employed in the separation system. They were a cupric oxide furnace (900°C) and a copper metal furnace (900°C) along with the titanium furnace (900°C). Figure 3 shows the thermal conductivity cell response as the sample was removed from the molecular sieve trap (trap III) at 0°C, giving a comparison of the effectiveness of the three furnaces for removing the interfering gases from the krypton. The titanium furnace was the best for removing the interfering gases from krypton; hence, it was incorporated into the separation system.

The reproducibility of ^{85}Kr in an environmental air sample was determined by performing six analyses on one tank of compressed air. The average concentration was $14.7 \text{ pCi } ^{85}\text{Kr}/\text{m}^3$ air at standard temperature and pressure with a 2- σ error of ± 7.2 percent. This concentration of ^{85}Kr in air is in good agreement with that predicted from the data of Shuping et al. [4].

It was necessary to mix the ^{83m}Kr spike with the air as opposed to introducing it into the charcoal trap (trap I) with the first part of the air being analyzed. The average recovery of ^{83m}Kr for two analyses was 85.5 percent when mixed with the air and 74.3 percent when not mixed with the air. The latter method of introducing the ^{83m}Kr spike would result in calculated ^{85}Kr concentrations higher than the actual concentrations. Employing the mixing technique the krypton recoveries normally range from 80 to 90 percent.

SUMMARY

A rapid method for determining ^{85}Kr in environmental air samples is described. The equipment and procedures are modifications of those presently being used to determine ^{85}Kr in gaseous samples. Air samples are spiked with ^{83m}Kr to provide a direct determination of the krypton separation yield. This feature eliminates the need for expensive analytical equipment, such as a mass spectrograph for determining the purity of the final separation and the uncertainty in measuring krypton volumetrically when small amounts of other gases are present. The system is essentially all metal which eliminates the breakage problems encountered with glass systems. A one cubic meter air sample can be processed in about four hours with a 2- σ error of less than 10 percent.

APPENDIX

Procedure for spiking air samples with ^{83m}Kr (Figure 1)

Open valves A, 1, 3, 4 and 5, and evacuate to less than five microns of mercury. Close valves 4 and 5, open valve 2 and allow the ^{83m}Kr to equilibrate for about ten minutes. Close valves 2, 1, A and 3. Open valves 11, 8, 7, 4 and 6, and start sample flow. Remove liquid scintillation vial (V_r) along with valve A and fill with

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liquid scintillation solution. The liquid scintillation solution and filling technique are described in a previous paper [5]. After the sample and spike have been transferred to the balloon, stop the sample flow and close valves 11, 8, 7, 4 and 6. The sample is now ready for introduction into the krypton separation system.

Procedure for separating krypton from the other air constituents (Figure 2)

I. Cool trap I with liquid nitrogen (LN). Start the spiked sample through trap I by opening valves 33, 34, 32, 30, 28, 9 and 11. Adjust the flow rate with needle valve C (approximately ten liters/min.). A wet test meter is connected to the exhaust vent of vacuum pump 2 to measure the volume of air passing through trap I.

A. To clean trap III open valves 41, 42, 44, 47 and 45, and heat with a wrap-around furnace for about an hour at 350°C. Remove the heat and close valves 41, 42, 47 and 45, and open valve 43. When the helium flow into trap III stops, close valves 43 and 44.

B. To clean trap IV open valves 21 and 20, and heat with a heat gun for about 15 minutes. Remove the heat gun and close valve 20. Open valves 43, 16, 15 and 13. After a few seconds, close valves 13 and 15, and open valve 17. After a few seconds close valve 17 and open valve 18. When the helium flow into trap IV stops, close valves 18, 16 and 43.

C. About ten minutes before the spiked air sample has completely passed through trap I, open valves 50, 43, 42, 26, 25, 12 and 13 to start the helium flow through the thermal conductivity cell (TCC). Adjust the helium flow rate (approximately 3 liters/min.) with needle valve D. With the helium flow rate adjusted, switch on the TCC electronics.

II. After the spiked sample has been removed from the balloon close valves 11 and 9 and warm the precoolers with a heat gun. Then close valves 28, 30, 33, 13, 12, 25, 26, 42 and 43. Open valves 31, 24, 12 and 13. Adjust the helium flow to three liters per minute with valve D. Remove LN from trap I and replace with a dry ice-acetone slush (DIA).

A. Open valves 41 and 40 about one minute then close. Heat trap II to 900°C.

B. Evacuate V_8 to less than 5 microns of mercury by opening valves 22, 23 and B.

C. Cool trap III with LN.

III. When the TCC reading returns to near the baseline setting, adjust the helium flow to one liter per minute. Close valve 13 and open valves 14, 38, 40, 42, 44, 45 and 46. Remove the DIA from trap I and replace with an electric wrap-around furnace and heat to 350°C to transfer the gases remaining in trap I to trap III. After about ten minutes close valves 46, 42, 40, 14, 12, 24 and 31.

IV. Shut off the furnace to trap II and open valves 33 and 36. After about a minute close valve 36. Continue heating trap I for about an hour at 350°C.

V. Cool trap IV with LN and open valves 43, 27, 25, 12, 15 and 17. Adjust the helium flow to about 100 cm³/min. Remove LN from trap III and replace with an ice water bath. Follow the TCC response and about a minute before the krypton appears, close valve 17 and open valves 18 and 19. After the krypton has been transferred from trap III to trap IV, close valves 19, 18, 15, 12, 25, 27, 45, 44 and 43. Turn off the TCC electronics.

VI. To remove the excess helium from trap IV close valve 22 and open valve 20 and evacuate to less than 5 microns of mercury. Close valve 21 and open valve 22. Remove LN from trap IV and cool scintillation vial V₈ with the LN. Heat trap IV with heat gun for five minutes. Close valves 23 and 20. Remove LN from the scintillation vial and warm to room temperature. Remove the scintillation vial along with valve 8 and fill with liquid scintillation solution. The time required to this point is about four hours.

VII. Count V₇ and V₈ for ^{83m}Kr. After the ⁸³Kr has decayed, count V₈ for ⁸⁵Kr.

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DISCUSSION

Naomi H. HARLEY: Does ²²²Rn present any problem in your measurement of the ⁸⁵Kr?

R.L. SHEARIN: No, it remains on the molecular sieve trap and comes off at a later stage, after the trap has been heated.

P. WINIGER: I should like to point out that over an activity range of ~1 µCi, for example the gas phase from a primary reactor circuit, ⁸⁵Kr can be detected with a Ge(Li) gamma spectrometer without special separation of the samples, although the intensity of the gamma transition at 514 keV is very weak.

R.L. SHEARIN: Yes, but in the general environment, concentrations are much less than this.